Perovskite Power

A breakthrough in the production of extremely low-cost solar cells may finally make possible cheap, abundant solar power for everyone.

SUNLIGHT IS ABUNDANT beyond the energy needs of the entire human race and completely free. Yet ironically, this free and abundant energy resource has long been deemed too expensive to harness. Photovoltaic panels, plus systems to make them compatible with grid electricity, plus batteries to squirrel away energy for when it's cloudy—all these add cost. And while such hardware and installation costs have diminished over time, the standard silicon solar cells they rely upon remained stubbornly expensive for most of the past quarter century.

In recent years, the picture has changed somewhat. Costs for silicon solar cells have dropped to the point where, in particularly sunny regions, solar energy can compete with higher-cost energy sources in the existing power mix. But these cost reductions have largely resulted from economies of scale, which may now have saturated. There is a sentiment within the industry that any future savings of significance will have to derive not from further manufacturing economies but from tangible scientific advances in solar-harvesting materials or their processing.

Solar-harvesting materials under development at Los Alamos and elsewhere include specialized thin films, organic layers, semiconductor nanodevices, and others. Each has promise, and each has drawbacks. But a new class of challengers emerged a few years ago and has been improving with surprising speed since then. Known as perovskites, they are any crystalline material with the same broad class of chemical structure as a natural mineral of the same name. Perovskite solar cells are generally easy to work with, easy to adjust for improved performance, and very easy to afford. And in recent experiments at Los Alamos, a particular recipe has been shown to reliably generate perovskite crystals that exhibit solar conversion efficiencies comparable to those of silicon.

"Silicon solar cells are still the gold standard. They're reliable and efficient, and they've been thoroughly demonstrated in the field," says Los Alamos materials scientist Aditya Mohite. "But I think we can do better."

Anatomy of a cell

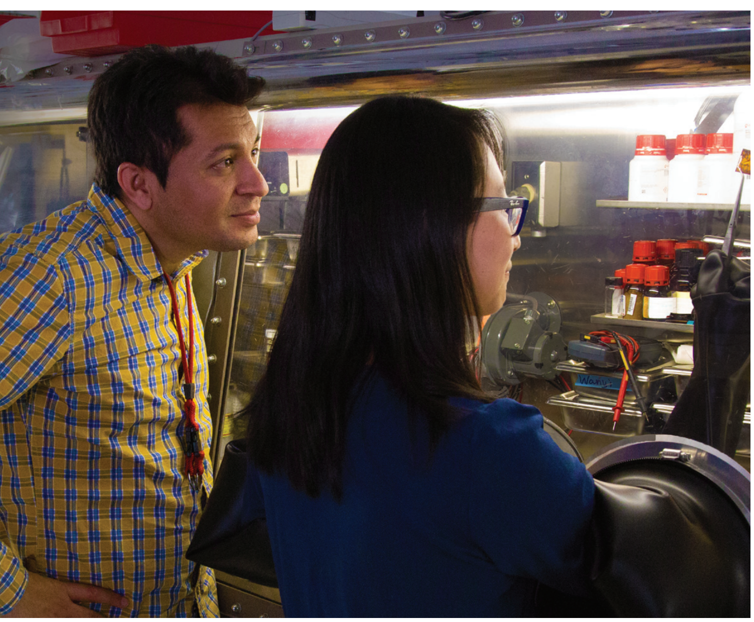
A standard solar cell contains an active layer, usually silicon, sandwiched between two electrode layers. Inside the active layer, photons of sunlight transfer energy to electrons in the material, allowing the electrons to break free from their normal energy state and enter a higher-energy state in which they can power an external circuit. This is known as the photoelectric effect, and in physics parlance, these photoelectrons are said to jump across an energy gap from the valence band to the conduction band. The gap between the two bands, or band gap, can be bigger or smaller in different materials, and in silicon it happens to be nearly ideal for solar power applications.

"At first glance, it would seem that the smaller the band gap the better, because then a greater percentage of solar photons would have enough energy to excite an electron up to the conduction band," explains Sergei Tretiak, a theoretical physicist on the Los Alamos team. "But then any excess energy a photon has beyond the band-gap energy is wasted." In this sense, a higher band-gap material might be preferred; although fewer solar photons would make the cut, less energy would be wasted by those that do. The combination of the two effects creates a sweet spot for photoelectric energy conversion. And after taking into consideration the selective atmospheric absorption of sunlight at different wavelengths, that sweet spot divides into two optimal peaks at about 1.1 and 1.4 electronvolts (eV) of energy. The silicon band gap is 1.1 eV, making it hard to beat (or even tie). The team's perovskite has a band gap of about 1.5 eV—slightly worse than silicon, but still better than a lot of other alternatives.

Once an electron jumps into the conduction band, all it has to do is move to the negative electrode without getting trapped somewhere along the way or encountering a positive "hole" left behind when another electron made the jump. Conventional silicon solar cells, dubbed first-generation technology, are typically 0.1 millimeters thick, so the photoelectron needs to travel at most that far to reach an electrode. The distance is even shorter in second- and third-generation, thin-film solar cells. The perovskite layer (third generation), for example, is only 500 nanometers (nm) thick, thus requiring 200 times less material (and correspondingly less weight) than first-generation solar panels. Yet even 500 nm can be a long way for a photoelectron to travel unimpeded in an imperfect crystal.

Huge millimeters

What makes silicon and other semiconductor solar cells so expensive to make is the required purity of their crystal structure. Even the most miniscule of crystal defects creates a natural electron-trapping site, so a solar-cell crystal must be extraordinarily free of defects for the photoelectrons to reliably reach the electrode. And sometimes reaching the electrode isn't enough; the interface between the active layer and the electrode layer can sometimes cause a photoelectron to rebound back into the crystal. These are the struggles associated with crystalline solar cells, and this is what Mohite is most enthusiastic about in the new Los Alamos crystals.



Aditya Mohite (left) and Wanyi Nie examine a newly produced perovskite crystal.

"We're growing crystals with millimeter-scale, defect-free domains," Mohite says. "That's unheard of. It virtually guarantees that the photoelectrons make it out." A millimeter may not sound like much, but the important point is that it's 2000 times greater than the 500-nm thickness of the solar cell. So an electron has to travel up to 500 nm, possibly multiple times due to rebounds at the electrode interfaces. But while doing so, it will almost never wander far enough sideways to reach a defect at the edge of the defect-free domain. The odds are overwhelmingly against that. As a result, the perovskite, while slightly worse than silicon in terms of its natural band gap, can be much more cheaply manufactured with excellent crystal purity.

The secret to the team members' success appears to reside in the way they have learned to process the perovskite. In particular, they use a technique called hot casting: coating an already hot substrate with the perovskite material in solution. And although this takes place at an elevated temperature, it is still a lower temperature (read: cheaper and easier) than that of comparable procedures for manufacturing other types of solar-cell crystals. The result is a surprisingly industry-adaptable crystal production process.

"Until now, growing solar crystals required high temperature or sophisticated processing," explains Wanyi Nie. Nie and Hsinhan Tsai are postdoctoral researchers on the team, and both have been instrumental in developing the new perovskite crystals in the lab. "But here we have low temperature and easy solution processing."

The solution aspect is a big deal. Unlike the complex crystal-growth methodologies used to make conventional, state-of-the-art semiconductor solar cells, solution processing is both fast and flexible. Fast means inexpensive, and the flexibility of liquid solution-based processing means the perovskite can be applied in convenient ways, such as spraying or painting the photoelectric layer directly onto a surface, opening the door to numerous new applications.

Solar sell

For commercial success, inexpensive, low-temperature solution processing is not enough. The new perovskite solar cells need excellent performance as well. That means they must be three things: efficient, predictable, and long lasting.

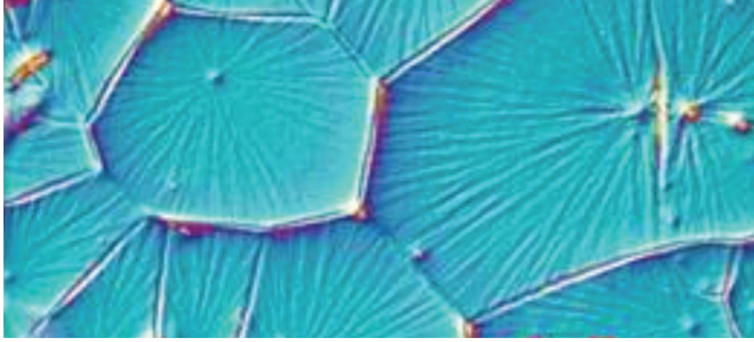
Silicon cells, while theoretically capable of 33 percent efficiency, have so far reached only about 20 percent in commercial use. In other words, they convert about 20 percent of the energy in sunlight into usable electricity. The most efficient solar cells to date are known as multi-junction solar cells, which combine two or more absorbers with band gaps optimized for different colors within sunlight. But as Mohite says, "Sure, multi-junction, NASA-quality solar cells can get you almost 40 percent, but they can't compete commercially. We're more than a thousand times less expensive."

To compete, perovskites need to come close to commercial silicon's 20 percent, and so far, the Los Alamos team is averaging 15 percent. Their current best is 18. Yet it took *decades* for silicon cells to reach 20 percent, and Los Alamos got perovskites to 15 percent in just six months.

"We haven't really tried to optimize our efficiency yet, either," says Hsing-Lin Wang, a Los Alamos chemist on the team. "We started with a generic perovskite and relatively common electrode materials. And our hot casting parameters, like evaporation rate and spin rate, are probably not ideal yet. All these things can be dialed in more carefully."

Their perovskite, for instance, has the chemical structure $CH_3NH_3PbX_3$, where the X at the end is a halide, such as chlorine, iodine, or bromium. Yet other materials that might perform better in various ways can be substituted at any part of that chemical formula. In particular, Wang believes they can adjust the material to lower the 1.5-eV band gap slightly and correspondingly increase the absorption of sunlight.

The electrode materials could improve, too. Their upper, positive electrode is made from indium tin oxide, a transparent conducting glass that lets sunlight through to the photoelectric layer. Their lower, negative electrode is made of carbon fullerenes, 60-atom carbon balls. These materials were chosen in part because their valence energies are very close to the corresponding perovskite energies. The carbon fullerenes have a valence energy just below the perovskite conduction energy, which helps to coax electrons from the perovskite into the electrode to power the circuit. The valence energy of the indium tin oxide lies just above that of the perovskite, nudging electrons back into the perovskite to complete the circuit. But with a different perovskite composition, these energy levels would change, and other electrode materials could take advantage of the new levels better than the current materials do. With such changes, efficiencies are likely to improve.



Los Alamos scientists reliably produce high-efficiency perovskite crystals like these that are free of defects on exceptionally large scales and are therefore resistant to losing or trapping valuable photoelectrons. The millimeter widths of such crystals greatly exceed their 500-nanometer thicknesses, making the photoelectrons exceedingly unlikely to encounter an edge defect before reaching the electrode layers above and below.

In terms of predictability, the Los Alamos perovskites are already exceptional. They have a very narrow range of efficiencies when produced. And their electrical performance is unusually simple. Most solar cells, including silicon, ramp up and down in voltage and current in complex ways. As a result, it is difficult to even determine (much less implement) their optimal voltage and current settings. The team's perovskites do not suffer from this problem.

The only real question is their longevity. Perovskites in general have not yet been shown to maintain their photoelectric efficiency for long periods of time when exposed to the environment. Indeed, oxygen and humidity tend to degrade them. So the perovskites still need to be properly engineered (or at least sealed, as silicon cells are) to avoid this problem. But this is unlikely to be a deal breaker, as the more difficult problems have already been largely overcome.

"Like silicon, our crystals absorb well across the solar spectrum, they're defect-free over large millimeter distances, and they can be made cheaply and easily," says Mohite. "And I'm confident our efficiencies will get close to the theoretical limits."

It might seem reasonable to take such claims with an element of skepticism. In spite of solar power's potential to rescue humanity from its energy woes, progress has been fraught with struggles and setbacks. Yet these new perovskites are showing much more promise, advancing much more quickly, and proving to be much more problem-free than the solar-energy field has come to expect. And to see the enthusiasm on the team's faces, one can't help but think they're on to something. LDRD

—Craig Tyler

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